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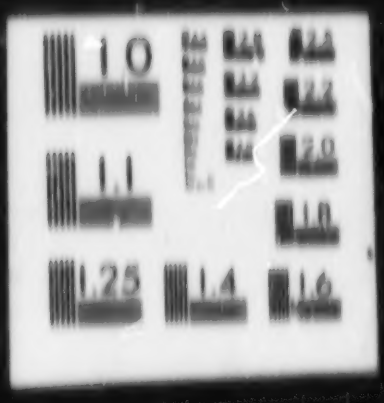

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Electrodialysis for Closed Loop Control of Cyanide Rinse Waters

Keystone Lamp Mfg Co, Slatington, Pa

Prepared for

Industrial Environmental Research Lab -Cincinnati, Ohio

Aug 77

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Full scale demonstration of electrodialysis for closed loop treatment of brass plating cyanide rinse waters was conducted in the Keystone Lamp Manufacturing plant at Slatington, Pa. In treatment of actual rinse water, the system was only one-quarter as effective as anticipated. Numerous attempts to improve the efficiency of the installation were unsuccessful and the work was terminated. Laboratory studies indicated that the failure was caused by a reduction in the permselectivity of the anion membranes. It is believed that an insoluble zinc compound or zinc complex anion was retained on the membrane and reduced its permselectivity. To avoid future failures, the membranes need to be laboratory tested on actual waste waters before a full-scale demonstration. In this study the electrodialysis system was tested on sodium copper cyanide solutions, whereas the actual rinse waters contained sodium copper zinc cyanide.

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ELECTRODIALYSIS FOR CLOSED LOOP CONTROL OF CYANIDE RINSE WATERS

by

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for

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The subject of the report was to evaluate a full-scale, closed-loop electrodialysis system for brass plating cyanide rinse waters. The system proved to be inefficient and therefore unsuitable for this application. To avoid future failures, this report stresses the importance of membrane testing in solution to be treated on a laboratory scale before a full-scale demonstration. For further information concerning this subject the Industrial Pollution Control Division should be contacted.

David G. Stephan
Director
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ABSTRACT

Full-scale trials of electrodialysis of brass plating rinse solutions were conducted in the plant of the Keystone Lamp Manufacturing Company at Slatington, Pennsylvania. The installation was intended to deplete dissolved salts in the rinse waters, thereby rendering the water suitable for re-cycle to the rinsing operations and returning the salts to the plating bath. Zero discharge would thus be achieved.

The system worked to a certain extent but was only about one-fourth as effective as had been anticipated from prior work in which electrodialysis was used to effectively treat sodium copper cyanide rinse waters. The reason for this was not immediately apparent, and considerable time was spent exploring various hypotheses of a mechanical or electrical nature.

Eventually it appeared that the inefficiency was caused by a reduction in permselectivity of the anion membranes as a result of retention of an insoluble zinc compound or of a tightly adsorbed zinc complex anion. No remedy that would not disturb the chemistry of the plating bath could be found for this situation, so the work was terminated.

The lack of success in this particular application should not discourage attempts to apply electrodialysis to other waste treatment processes. Small-scale preliminary tests should be made, however, if there is any question about the interaction of membranes and dissolved salts.

This report was submitted in fulfillment of Grant No. S-803304 by Keystone Lamp Manufacturing Company under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 1, 1974 to December 31, 1975, and work was completed as of January 12, 1976.

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We thank Asahi Glass Company, Ltd., for the opportunity to use their excellent electrodialysis cells in this application.

SECTION I

INTRODUCTION

In January 1973, International Hydronics Corporation, Princeton, New Jersey, entered into an agreement with Dr. Sidney J. Tuwiner, New York, to develop and market Dr. Tuwiner's process for the concentration of electrolyte from dilute washings by electrodialysis in a closed system as described in his U.S. Patent No. 3,674,669, July 4, 1972, and (later) in his report "Investigation of Treating Electroplaters Cyanide Waste by Electrodialysis", EPA-R2-73-207, December, 1973.

As applied to an electroplating line, the Tuwiner process operates as follows. The first rinse solution is circulated through the depleting chambers of an electrodialysis stack, and the bath solution is passed through the concentrating chambers of the same stack. The second rinse solution is passed through the depleting chambers of a second electrodialysis stack, and the first rinse solution is put through the concentrating chambers of the second stack. Salts are thereby transferred from the second rinse to the first rinse, and from the first rinse to the bath. The concentration of the rinse solutions is thus maintained at a low enough level that they can be continuously recycled and accomplish the desired rinsing effect while the plating salts are returned to the bath. A schematic flow diagram is shown in Figure 1.

The Tuwiner process has the evident advantages, first, that waste rinses containing polluting materials do not have to be treated prior to discharge since there will be no discharge and, second, that valuable chemicals and process water will be conserved.

It is well known that in order for a multichamber electrodialysis stack to achieve the greatest possible efficiency in depleting the salt concentration of one stream while increasing the concentration of the other, it is necessary to eliminate or at least minimize any cross-leakage of the two streams within the stack. Dr. Tuwiner indicated that he felt an improvement in this feature of stack construction was needed, and International Hydronics began to design, fabricate, and test various configurations early in 1973.

The design ultimately adopted consisted of forty PVC frames 0.159 cm thick with an open area of 0.074 square meters. On each side of a frame was a pure gum rubber gasket 0.079 cm thick. Anion and cation membranes were MA-3475 and MC-3470, manufactured by Ionac Chemical Co., Birmingham, N.J. The construction of the channels leading from the manifolds into the chambers was subsequently found to be very similar to that described in Patent Nos. 3,219,572 (1965) and 3,235,481 (1966) assigned to A.M.F. by the inventor R. M. Zwart, Jr., although Hydronics was unaware of these patents at the

time. Cross-leakage within a 40-chamber stack of this design amounted to less than 5 cc per minute at a pressure differential between chambers of 0.14 kg/sq cm and at a flow rate through one set of chambers of 22.7 liters per minute.

Stacks of this type were tested in the Hydronics' pilot plant on sodium copper cyanide solutions during the latter part of 1973. What the Tuwiner process refers to as "first stage" operation-depletion of ions from a first rinse with corresponding transfer of ions to a bath solution-was simulated using a "bath" solution of 60,000 to 70,000 ppm total cyanide. The "first rinse" solution was typically depleted to 0.02 of those concentrations when the drag-out from "bath" to "rinse" was 3.79 liters per hour. The flow rate of both streams was about 37.85 liters per minute; the pressure of the depleted stream was maintained about 0.14 kg/sq cm higher than that of the concentrated stream. Voltage applied to the stack was 125 volts; amperage was 25-40 amps, depending on temperature.

Similarly, "second stage" operation was studied using a "first rinse" of 600-700 ppm total. Using the same stack and a 3.79 liters per hour drag-out rate, the depleted stream ("second rinse") was again maintained at 0.02 of the concentrated stream. The amperage was about 0.3 amps at an applied potential of 125 volts across the stack.

In general, the performance of the stacks described above was felt to confirm Dr. Tuwiner's findings in a cell of fewer chambers as reported in the above-mentioned EPA report.

At this stage, Hydronics wanted to find a plating plant that would permit installation of the system and testing under actual operating conditions. A particular aim was accumulation of data on the life expectancy of the membranes. Hydronics was fortunate to be given the opportunity to conduct such trials at the Slatington, Pennsylvania plant of the Keystone Lamp Manufacturing Company. The solutions to be treated were the first and second rinses following a typical brass bath in a continuous, automatic plating line. At the time, it was assumed that a sodium copper zinc cyanide solution would behave just as had a sodium copper cyanide solution in our pilot runs. The equipment was installed at Keystone in February, 1974.

During the next 2 months, the system was run during the normal 8-hour shift on 16 days. Performance was poorer than expected to the extent that the rinse concentration rose steadily instead of being depleted or being held at a constant low value. This was blamed in part on various mechanical and chemical problems which were encountered and corrected, and in part on the assumption that the drag-out rate was much higher than the system had been designed to handle: 3.79 liters per hour.

Problems of electrode corrosion, buildup of brass on the first stage cathode requiring frequent removal, and precipitation of copper and zinc cyanide (particularly in the second stage depletion chambers) were especially troublesome and required a major reorientation of our concepts.

The stacks were returned to Hydranautics' pilot plant for revision. Platinized titanium electrodes were installed at both ends of the stacks instead of stainless steel. Switches were provided to reverse the polarity of the potential applied to the stacks, and three-way valves were installed to interchange the depleted and concentrated streams. These measures permitted daily potential reversal and stream interchange and solved the above-mentioned problems.

It was this system that was in operation when the present EPA grant went into effect on July 1, 1974. The grant was to extend to January 31, 1975, and was to provide for accumulation of data indicating the reliability of the system, the life of the membranes, and the economics of the process.

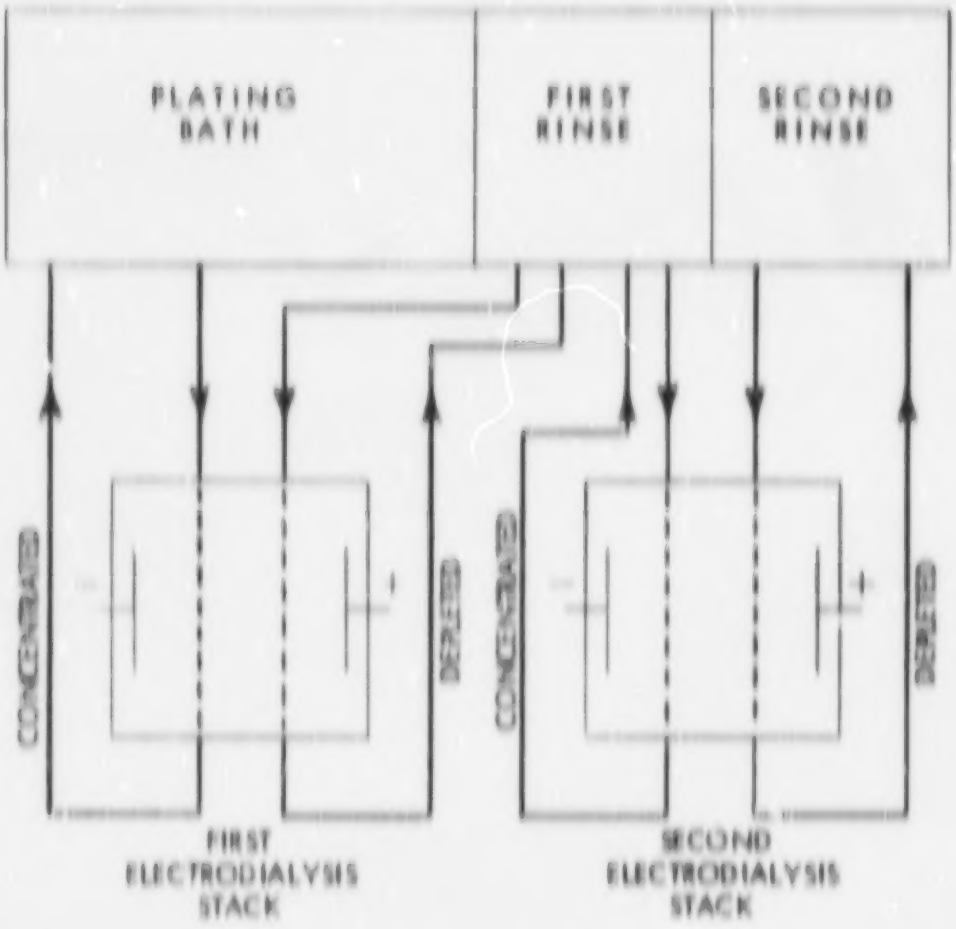

Figure 1. Schematic flow diagram of electrodialysis of electroplating rinse waters.

SECTION 9

CONCLUSIONS

From extended plant trials of electrodialysis of brass plating rinse waters for return of chemicals to the bath and demineralization of the rinses for reuse, the following conclusions were drawn:

1. The electrodialysis of brass solutions carried out under plant conditions was only about one-fourth as effective as that achieved with sodium copper cyanide solutions in prior inhouse pilot plant studies.

2. Various possible mechanical and electrical malfunctions were ruled out as causes of this inefficiency.

3. Two sets of electrodialysis stacks, one developed by International Hydronics Corporation, the other manufactured by Asahi Glass Company, Ltd., differing primarily in chamber design, performed similarly.

4. Increasing the membrane area by using two stacks in parallel on the first rinse did not improve delonization rate.

5. Laboratory experiments indicated that the inefficiency of brass solution electrodialysis could be attributed to retention of some insoluble zinc compound or complex ion on the anion permeable membranes, thus reducing their permselectivity.

6. In view of the unsatisfactory performance for this particular application, it was considered unwarranted to continue trials for a longer period which would have been necessary to fulfill the original aims of the U.S. Environmental Protection Agency (EPA) grant: establishment of system reliability, membrane life, and economics.

SECTION 3

RECOMMENDATIONS

Before undertaking full-scale trials in the future, it would be well to determine the permselectivity of membranes in the solutions to be used and to conduct small-scale, three-chamber cell tests as described in this report.

The experience described in this report on the electrodialysis of actual brass solutions should not discourage further attempts to apply the principle to other rinse streams. The potential for conserving chemicals and water and attaining zero discharge remains very great.

SECTION 4

DEVELOPMENT AND DEMONSTRATION STUDIES

INTERNATIONAL HYDRONICS ELECTRODIALYSIS CELLS

When the present EPA grant became effective on July 1, 1974, the system in operation at the Keystone Lamp Manufacturing Co. was essentially as previously described and shown in Figure 2 with certain exceptions as follows.

1. The first stage stack consisted of 80 chambers (40 cell pairs) and the second stage stack of 40 chambers (20 cell pairs). The increase in chambers in the first stage had been made in order to reduce amperage which was causing overheating of this unit.

2. The simple, two-way valves (V-1 c, V-1 d, V-2 c, V-2 d, etc.) were replaced with three-way valves which were interconnected in such fashion as to permit interchanging the depleted and concentrated streams in each stage on a daily basis.

3. The rectifier was connected to the electrodes through double-pole, double-throw switches so that the polarity could be reversed at the same time the streams were interchanged.

Operation with the electrodes having a certain condition of polarity and the concentrating and depleting streams flowing through the proper chambers was said to be "Forward" operation. The reversal of polarity and the corresponding interchange of streams was said to be "Reverse" operation.

It is to be noted that the concentrated stream for the first stage was contained in a separate recirculating drum independent of the actual plating bath. This permitted the study of different concentrations in this stream and also allowed for checking the suitability of this solution for return to the plating bath by withdrawing a sample for Hull cell tests. In the first stage the solution from the recirculating drum was passed through the electrode chambers in two separate streams. In the second stage, the first rinse was passed through the anode chamber, and the second rinse through the cathode chambers.

Previous experience at Keystone had shown that the inefficiency of the system could be compensated for by transferring part of the rinses into the plating bath each morning. Daily evaporation from the plating bath was of such magnitude that about half of the first rinse could be transferred to the bath as makeup. The same volume of second

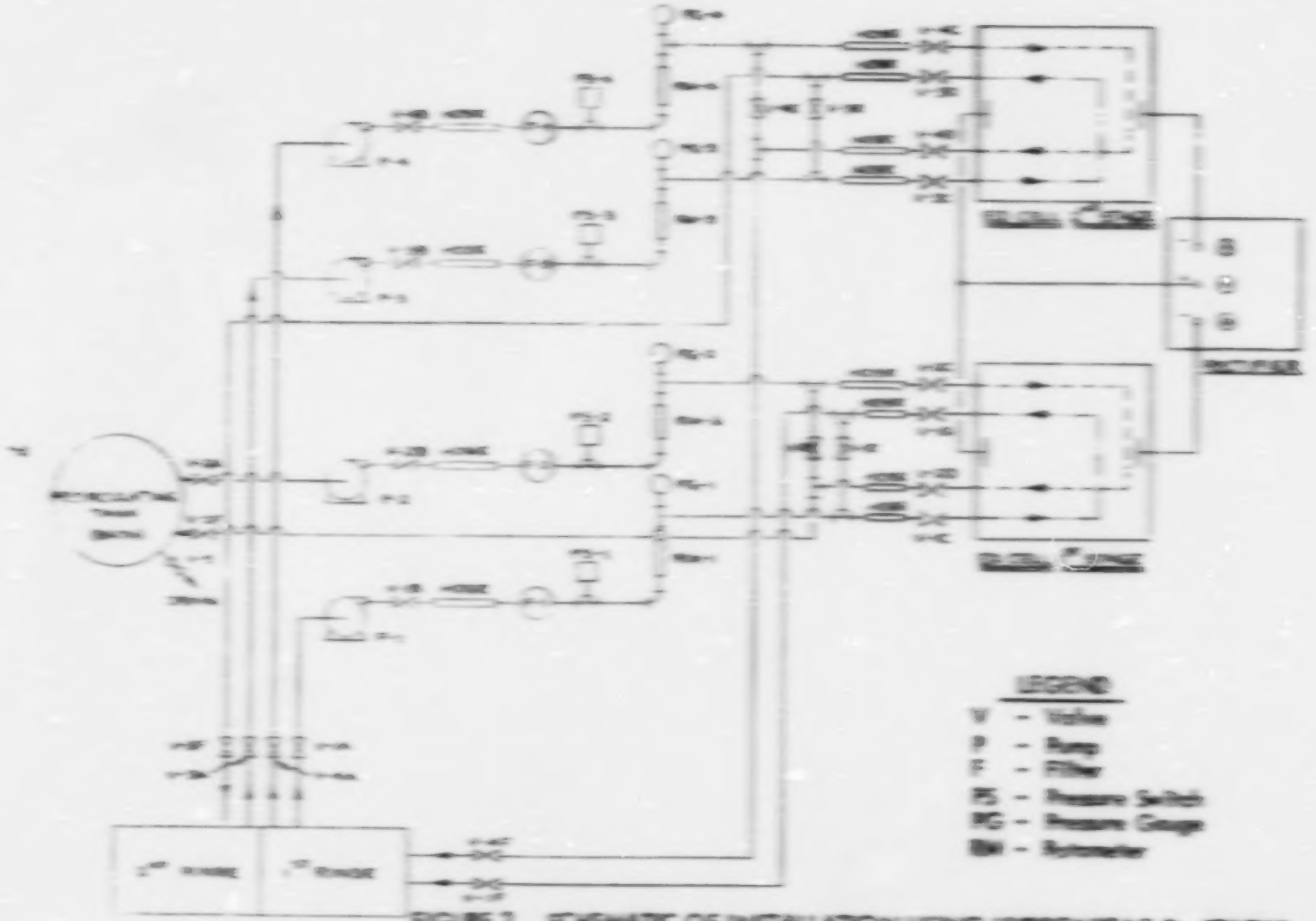

FIGURE 2. SCHEMATIC OF INSTALLATION USING HYDRONICS E.D. STACKS

rinse was then transferred to the first rinse tank. The second rinse tank was then filled with softened water. In previous runs the electrodialysis system transferred enough salts out of the rinse streams that the second rinse was held at an acceptably low concentration for the subsequent plating operation that the parts were subject to.

A typical day's operation covered the regular 8-hour shift in the plating department. The three-way valves and the double-pole, double-throw switches were set for the opposite direction of the previous day's run. All pumps and the rectifier were turned on simultaneously by means of a single "start" button on a central control panel. On data-logging forms the following information was recorded: time, first and second stage amperage, volts, flow rates in gpm for all streams (from rotameters), pressure in psi in all streams (from pressure gauges), the temperature of the solutions in the recirculating drum and both rinse tanks, and the conductivity of all solutions. These data were collected periodically throughout the day's run and at shut-down.

Conductivity had been related to total cyanide concentration by analysis of suitable solutions over a wide range of concentration. For concentrations in the range of the recirculating drum (20,000-70,000 ppm) the solutions were diluted 1:200 with distilled water to get them into a suitable range on the conductivity meter. Similarly, first rinse solutions (1000-7000 ppm) were diluted 1:20 while second rinse solutions were measured without dilution.

Forty-four runs were made with the system as described above. In nine cases the data were not complete. For the other 35, the most relevant data are presented in Table 1. Certain parameters in these runs were fairly constant and fell in the ranges indicated as follows.

Flow rate:

First stage, both streams ..... 37.85 to 49.21 liters per minute

Second stage, both streams ..... 30.28 to 37.85 liters per minute

Pressure of feed streams:

First stage ..... 1.26 to 1.48 kg/sq cm

Second stage ..... 1.26 to 1.48 kg/sq cm

(Depleted streams were maintained at the same pressure as the concentrated stream in the same stack or at pressures up to 2 psi higher than the concentrated stream).

TABLE 1. HYDRONICS STACKS: 80 CHAMBERS IN FIRST STAGE, 40 CHAMBERS IN SECOND STAGE

Run Number	Test Hours	Amperes S1	Amperes S2	Rec. Drum Ave. Conc.*	First Rinse Conc.* Start	First Rinse Conc.* Finish	First Rinse Conc.* ppm/hr.	Second Rinse Conc.* Start	Second Rinse Conc.* Finish	Second Rinse Conc.* ppm/hr.
1	7.00	36-38	12 -9.0	43,000	7200	6800	229	440	380	- 8.6
2	6.33	36-36	4.5-4	41,000	3600	4000	190	145	140	- 0.8
3	6.75	35-38	5.5-4	41,500	5000	3800	178	170	180	+ 1.5
4	6.83	23-32	2.5-3.5	40,000	1650	3500	271	70	78	+ 1.2
5	6.25	28-25	2.5-3	40,500	1750	2750	162	75	62	- 2.1
6	6.00	18-27	2 -2.5	41,000	1045	2900	310	45	53	+ 1.3
7	4.33	25-30	2 -3	44,000	2200	3000	185	70	100	+ 6.9
8	5.83	25-35	2.5-3	44,000	2300	3600	257	80	89	+ 1.5
9	5.83	18-20	2 -3.5	47,000	2800	3600	172	110	110	0
10	5.67	15-18	1 -2.5	43,000	1400	3000	248	40	70	+ 3.7
11	6.17	15-18	2 -3.5	45,000	1360	3400	332	55	96	+ 7.1
12	5.55	21-27	2 -3	33,000	2300	3300	234	73	85	+ 2.2
13	4.75	17-20	2.5-3	34,500	1400	1940	97	62	70	+ 1.7
14	5.25	18-24	2 -3.5	35,000	1640	2800	221	60	65	+ 1.0
15	6.17	29-33	2 -2.5	50,000	1900	3000	178	44	56	+ 2.3
16	5.25	35-40	3.5	51,000	4300	4800	95	105	100	- 1.0
17	4.92	25-31	2 -4	47,500	3800	4200	81	30	70	+ 6.5
18	5.67	32-36	3 -4	49,500	3700	4600	159	100	115	+ 2.7
19	5.33	25-28	3	49,500	3240	4200	189	70	87	+ 1.7
20	4.83	17-21	2	33,500	2120	3000	198	67	68	+ 0.2
21	4.92	20-25	2 -3	32,000	2300	2900	163	60	77	+ 1.4
22	6.08	17-19	3 -4	30,500	2500	4200	296	105	140	+ 9.8
23	6.00	16-20	3	32,000	2400	4000	267	95	115	+ 3.3
24	5.67	16-18	3 -4	29,500	2400	3900	266	105	140	+ 6.2
25	4.42	22-24	3.5	44,000	3400	4300	794	120	100	- 2.7
26	7.83	15	3 -4	44,000	2100	4700	333	72	140	+ 8.7
27	7.58	14-15	2 -2.5	51,000	1045	3900	387	31	97	+ 7.5
28	7.83	9-13	2 -2.5	26,700	1160	4300	375	42	140	+ 12.5

(continued)

TABLE 1—Continued. HYDRONICS STACKS: 80 CHAMBERS IN FIRST STAGE, 40 CHAMBERS IN SECOND STAGE

Run Number	Test Hours	Amperes S1	Amperes S2	Exc. Drum Ave. Conc.*	First Rinse Conc.* Start	First Rinse Conc.* Finish	First Rinse Conc.* ppm/hr.	Second Rinse Conc.* Start	Second Rinse Conc.* Finish	Second Rinse Conc.* ppm/hr.
29	7.67	7–11	2 –3	18,000	2100	3700	239	86	112	+ 3.4
30	7.42	8–11	1.5–3	21,300	1740	3700	264	55	105	+ 6.7
31	8.08	7– 9	2.5–3	16,500	1300	3400	322	50	110	+ 6.4
32	7.67	10	3 –3.5	28,000	2800	4300	196	83	140	+ 7.4
33	7.83	9–11	3 –4	31,500	2100	3400	230	77	105	+ 3.6
34	7.25	10–22	2 –2.5	39,500	1500	3600	290	52	110	+ 8.0
35	7.83	13–15	2.5–3.5	59,000	1745	3600	238	77	125	+ 6.1
No diagonal	7.5	7–10	3 –2	25,000	3700	2200	– 66.7	112	32	– 10.7

* Concentration in ppm total cyanide.

Temperatures:

Recirculating drum ..... 80 to 117° F

First rinse tank ..... 90 to 114° F

Second rinse tank ..... 74 to 110° F

(Temperatures depended partly on ambient temperature; concentration of streams, which had some effect of amperage; and whether or not cooling was applied to the recirculating drum by means of a cooling coil. Temperatures rose 5 to 15° F during a run).

Voltage:

Both stages ..... 125-130 volts

Variations within the ranges of the above parameters were not observed to influence the performance of the installation in a systematic way; therefore the corresponding data on individual runs is not shown in Table 1.

The actual hours elapsed between the first and last sample is tabulated as "Test Hours", although the runs usually continued throughout the entire plating shift, 8.5 hours. Amperage in each stage is given at the time of the first and last sample.

The concentration of the recirculating drum is given as an average value. Although this concentration usually rose by 1000 to as much as 5000 ppm, such increases frequently did not correspond to transfers out of the first rinse stream and seemed to be due to evaporation.

The total cyanide concentration of the first and second rinse streams at start and finish was tabulated and the changes in that concentration per hour, "Δ ppm/hr", was calculated. This latter value is of interest when compared to drag-out rates, and to the operation of the installation when there was no drag-out, as discussed later.

In order to investigate the effect of the number of chambers in a stack, the first stage was reduced from 80 chambers to 44 chambers, the second stage remaining at 40 chambers. The flow rates in the first stage were now in the range of 34 to 45.4 liters per minute while the pressure on the feed streams, the temperature experience, and the voltage were essentially as described previously. The other data obtained during four runs with this assembly are given in Table 2.

Of prime interest were actual measurements of drag-out in the Keystone brass plating line when it was running normally and when the electrodialysis equipment was not in operation. This information was collected on eleven different days and is tabulated in Table 3.

TABLE 2. HYDRONICS STACKS: 44 CHAMBERS IN FIRST STAGE, 40 CHAMBERS IN SECOND STAGE

Run Number	Test Hours	Angeres S1	Angeres S2	Rec. Drum Ave. Conc.*	First Rinse Conc.* Start	First Rinse Conc.* Finish	First Rinse Conc.* ug/cm²/hr.	Second Rinse Conc.* Start	Second Rinse Conc.* Finish	Second Rinse Conc.* ug/cm²/hr.
36	7.83	17-26	1 -2	38,500	1680	2400	+ 92	35	60	+ 3.8
37	7.67	18	1.5-2.5	37,500	1260	3000	+ 207	39	77	+ 4.7
38	8.00	36-42	2 -2.5	37,500	1680	3000	+ 203	48	84	+ 4.0
39	7.33	18-28	2 -3	42,000	1540	3500	+ 267	39	87	+ 6.5

* Concentration in ppm total cyanide.

TABLE 3. DRAG-OUT IN KEYSTONE BRASS PLATING LINE

Run Number	Hours	First Rinse Conc.*			Second Rinse Conc.*			Calc. D-O gal.[a]
		Start	Finish	Δ ppm/hr.	Start	Finish	Δ ppm/hr.	
1	5.5	2,100	3,900	327	–	–	–	1.33
2	7.75	2,160	3,400	160	–	–	–	0.64
3	7.5	3,100	4,300	160	–	–	–	0.64
4	7.5	7,300	7,500	67	–	–	–	0.27
5	7.5	7,600	9,200	213	–	–	–	0.87
6	7.5	9,600	11,400	240	–	–	–	0.98
7	7.5	11,400	13,100	227	–	–	–	0.92
8	7.5	700	3,000	294	34	150	15.5	1.2
9	7.5	940	3,400	328	47	170	16.4	1.33
10	7.5	1,160	3,900	366	65	215	16.7	1.49
11	7.5	2,100	4,220	280	–	–	–	1.14
Average	–	–	–	242	–	–	16.9	0.98

* Concentration in ppm total cyanide.

[a] Calculating drag-out from 34,300 ppm total cyanide bath into 280 gal. first rinse tank at 1 gph would give a rise of 246 ppm CN/hr. in that tank.

Only one opportunity presented itself to determine the way in which the Hyen installation (with 80 chambers in the first stage and 40 chambers in the second)functioned in the absence of any drag-out, i.e., when the plating line was not in operation. This run was made following Run 29, Table 1. The pertinent data are given in Table 1 and discussed hereafter.

ASAHI GLASS COMPANY, LTD., ELECTRODIALYSIS CELL

Asahi Glass Company, Tokyo, Japan, generously loaned International Hydronics two of its Model DW-O electrodialysers for testing in the brass rinse application. Each of these units had the following characteristics.

Fifty concentrating chamber frames; 49 depleting chamber frames.

Frames 2 mm thick, made of resilient rubber. Open area 511 sq. cm.

Distributors leading from feed manifolds into chambers made of multi-tubular polypropylene.

Cation exchange membranes: Selemion CMV; Anion exchange membranes: Selemion AMV (products of Asahi Glass Co.).

Electrode chambers fed with streams different from those passing through the main portion of the stack.

Stainless steel cathode and anode.

These cells were tested hydraulically by passing water through one set of chambers and looking for the emergence of water from the other set of chambers; no internal cross-leakage was observed. One of the stacks was tested for electrodialysis of sodium-copper-cyanide solutions in the Hydronics pilot plant, and was found to deplete a simulated first rinse solution while a "bath" solution was being dragged into it at a rate of 3.79 liters per hour. Performance here was comparable to that found with the Hydronics stacks mentioned in the Introduction.

On the strength of these tests, the two Asahi DW-O stacks were installed at Keystone on the brass plating line in place of the Hydronics stacks. The system is sketched in Figure 3. It is seen that separate streams are fed to the electrode chambers in both stages. In the first stage, solutions of 52.4 gm NaCN/liter were recirculated to both electrodes; in the second stage, solutions of 7.49 gr NaCN/liter were used.

Three runs were made, and the data are tabulated in Table 4.

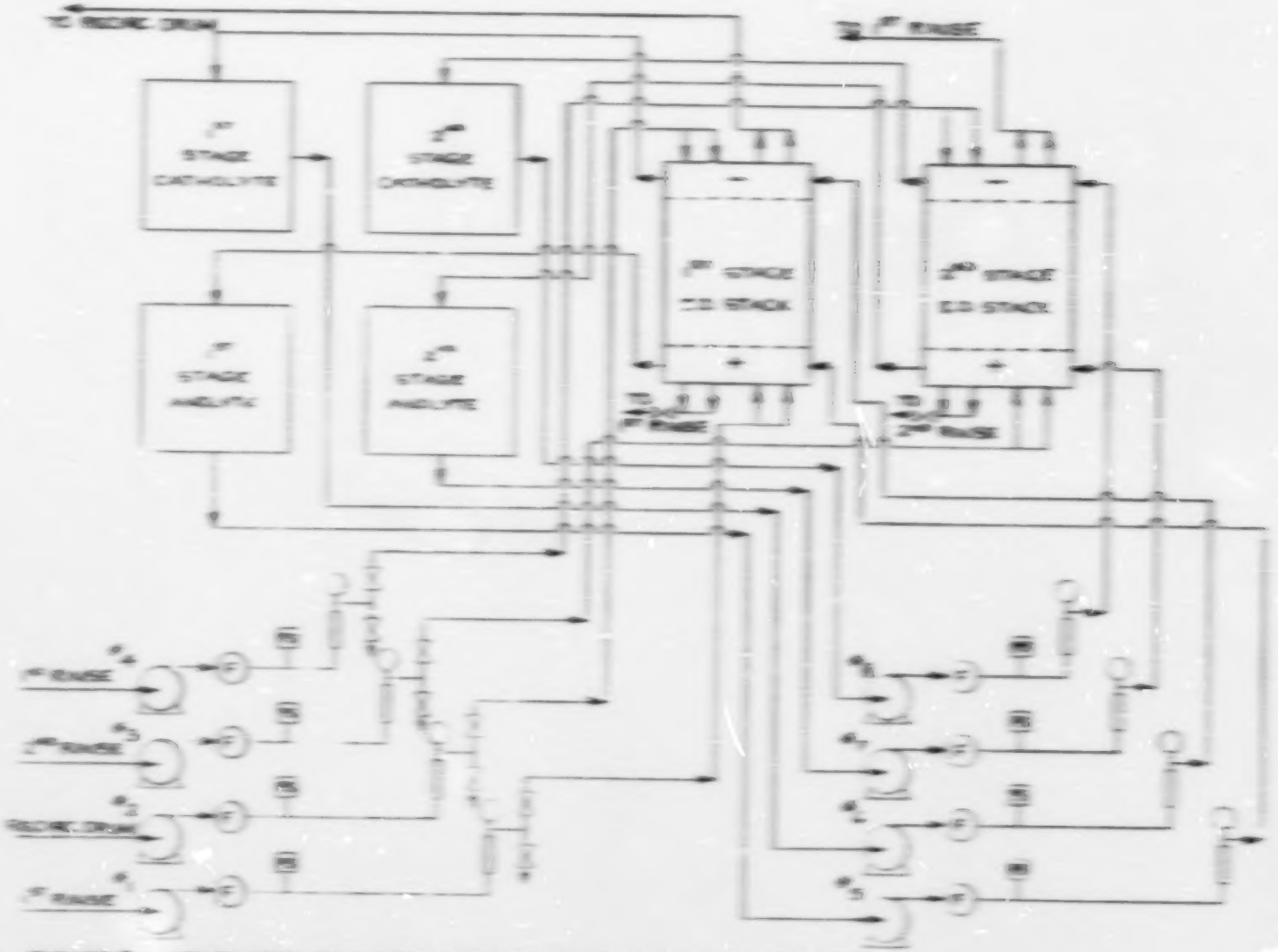

FIGURE 3. SCHEMATIC OF INSTALLATION USING ASAHI E.D. STACKS

TABLE 4. ASAHI STACKS: 99 CHAMBERS IN BOTH STAGES

Run Number	Test Hours	Amperes S-1	Amperes S-2	Rec. Drum Ave. Conc.*	First Rinse Conc.* Start	First Rinse Conc.* Finish	First Rinse Conc.* Δ ppm/hr.	Second Rinse Conc.* Start	Second Rinse Conc.* Finish	Second Rinse Conc.* Δ ppm/hr.
1	4.58	9-10	4 -4.1	54,000	33,000	26,000	- 1530	175	490	+ 66.6
2	8.38	10-12	4 -4.8	54,000	17,400	19,000	+ 198	350	640	+ 35.9
3	7.67	9-10	3 -4	54,000	11,000	12,800	+ 228	290	440	+ 19.1

* Concentration in ppm total cyanide.

TABLE 5. ASAHI STACKS: BOTH STACKS IN PARALLEL, OPERATING AS FIRST STAGE

Run Number	Test Hours	Amperes S-1	Amperes S-2	Rec. Drum Ave. Conc.*	First Rinse Conc.* Start	First Rinse Conc.* Finish	First Rinse Conc.* Δ ppm/hr.
1	4.33	10	13-15	54,000	12,200	12,900	+ 720
2	6.17	8-10	15	47,000	6,900	9,200	+ 385

* Concentration in ppm total cyanide.

When it appeared that the performance was tending in the same direction as that of the Hydrontics stacks, the second stage Asahi stack was re-piped so as to treat the solutions in the recirculating drum and the first rinse tank (separate solutions of 52.4 gm. NaCN/liter were now recirculated to these electrode chambers also). Thus both stacks were now arranged to function in parallel in "first stage" operation. The effect was that of doubling the cross-sectional area of exposed membrane without decreasing voltage per cell pair (one depleted and one concentrated chamber) and performance should have been materially improved. The data for two runs is given in Table 5.

LABORATORY INVESTIGATIONS

As it became apparent that electrodialysis of brass solutions proceeded less efficiently than that of sodium copper cyanide solutions, explanations were sought by means of various laboratory experiments.

Analysis of Anion Permeable Membrane from Brass E.D. Cell

A sample from one of the anion exchange membranes from the Hydrontics first stage stack when it was cut down from 80 chambers to 44 chambers (after 45 days of operation) was analyzed for its copper and zinc content. The membrane was washed thoroughly in distilled water and then cut into pieces about 0.318 cm square. These were digested in concentrated HNO_3 until only a scanty, granular residue, presumably the fluorocarbon binder, was left. The acid extract was diluted with distilled water and the solution analyzed by atomic adsorption spectrophotometry for copper and zinc. Brass plating solution was also analyzed for copper and zinc for comparison.

Membrane Resistance in Copper Cyanide and in Brass Solutions

A small PVC cell, built in two halves, was used for simple measurements of the resistance of membranes while direct current was passing through them. A steel cathode and a graphite anode were used. The cross-sectional area of the cell was 12.7 cm wide x 7.62 cm deep (96.62 sq cm), and the electrodes were 1.91 cm apart.

The cell was first filled with the solution of interest - either a sodium-copper-cyanide solution or a sodium-copper-zinc-cyanide solution. (In both cases, the solutions used contained approximately 60,000 ppm of total cyanide). Voltage from a small rectifier with voltage continuously variable from 0-15 volts was applied and was raised so as to make potential readings at 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.5, and 5.0 amperes. The entire course of readings was made in 2 minutes in order to minimize as far as possible the changes in composition and concentration which occurred as a result of electrode reactions.

The second step was to insert, between the two halves of the cell, an ionac membrane which had previously been equilibrated with the desired solution by soaking

in that solution for two days. The voltage-amperage readings were repeated as before. The data were plotted on coordinate graph paper in order to facilitate a qualitative evaluation of the possible interaction of membranes and ionic species.

Small, Three-Chamber Cell Tests of Electrodialysis

The same PVC cell described above, but modified to provide a 0.635 cm thick center chamber, was used to conduct some simplified electrodialyses on cyanide solutions. In these experiments, an Ionac cation permeable membrane was placed on the cathode side and an Ionac anion permeable membrane on the anode side, both membranes having been previously equilibrated for two days by soaking in plating bath solutions of interest. The bath solutions were placed in the electrode compartments, while 200 cc of a mixture made by diluting the bath 1:50 with distilled water was placed in the center chamber. The voltage was set at 12 volts. Amperes were read periodically, and the run was terminated when the amperage fell to 0.3 amps or less. The center chamber was analyzed at the start and at the end, and ampere efficiencies were calculated.

SECTION 5

RESULTS AND DISCUSSION

PERFORMANCE OF HYDRONICS STACKS ON KEYSTONE BRASS PLATING RINSES

From the very outset, the installation was incapable of depleting the first rinse fast enough to keep up with the drag-out rate. Table 1 shows increases in concentration of the first rinse from start to finish ranging from a low of 81 ppm/hr (Run 17) to a high of 382 ppm/hr (Run 27). Run-to-run variation could not be readily attributed to any one of the following parameters.

1. Flow rate of the streams.
2. Pressure in the feed lines.
3. Temperature.
4. Amperage (which is a function of applied voltage, temperature, and stream concentrations).
5. Absolute concentration.
6. Concentration differential between concentrated and depleted streams.
7. Whether the stacks were operating in "forward" or "reverse" fashion.

It is believed that the day-to-day variation in performance was primarily related to drag-out variation. Over a period of several weeks Keystone made available the figures on square meters of parts plated per day. However, it developed that these figures could not be related to degree of depletion either, and it is obvious that the shape of parts (whether flat or cup-shaped) is as important as simple projected area in determining the amount of drag-out. We have not attempted to quantify this shape factor because of the great variety and complexity of shapes plated on this line.

The above comments generally apply to the second stage performance, also. However, the second stage stack appeared to be depleting the second rinse somewhat more effectively. Five runs actually resulted in over-all decreases in concentration during the operating period.

Run Number	Δ ppm/hr
1	-8.6
2	-0.8
5	-2.1
16	-1.0
25	-2.7

Run No. 9 showed the same concentration at start and finish. However, the other 29 runs showed increases in second rinse concentration ranging from 0.2 (Run No. 20) to 12.5 ppm/hr (Run No. 28).

The 80-chamber (first stage) stack at 125 volts resulted in approximately 3 volts per unit cell. Much of the prior work (including some of Tuwiner's) was carried out at about 6 volts per unit cell. The latter condition, of course, provides a higher potential over the back-EMF due to concentration differential. In order to see if this would have significant benefit, the first stage Hydronics stack was reduced to 44 chambers, while the second stage stack remained at 40 chambers.

The data for four runs collected with this configuration, shown in Table 2, reveals essentially the same performance as found with the larger first stage stack. The range of concentration increases observed during these runs may be summarized in the following table:

TABLE 6. RANGES OF CONCENTRATION

Run Number	Δ ppm/hr	
	First Rinse	Second Rinse
36	93	5.8
39	267	6.5

During most of the work described above we were not alerted to the true state of affairs for two reasons.

1. From a practical standpoint, it was possible to maintain the second rinse at an acceptably low level by transferring part of the rinses toward the plating bath each day as described in the Experimental section.

2. It was assumed that the drag-out greatly exceeded the design capability of 3.79 liters per hour.

On two different occasions, the electrodialysis system was shut down for several days for inspection of the stacks and servicing of auxiliary equipment such as pumps and filters. During these periods the drag-out was measured by sampling the rinse tanks near the beginning and end of each shift. The resulting data are shown in Table 3 and indicate considerable day-to-day variation in concentration rise. However, the average was 242 ppm/hr. If one calculates the increase in concentration of the first rinse solution on the basis that 3.79 liters per hour of bath containing 64,000 ppm total cyanide is dragged into the first rinse tank, the volume of which is 984 liters, a rise of 1/260 x 64,000 = 246 ppm CN/hr would be anticipated. Thus, the average drag-out rate is in the electrodialysis system's design range of 3.79 liters per hour, and on only three days did the drag-out appreciably exceed that rate.

It is of interest to note that, in this line, it might be possible to maintain the second rinse at a sufficiently low concentration, without electrodialysis or other treatment, simply by starting with water in the first rinse tank, and, each day thereafter, pumping as much of the first rinse into the plating bath as evaporation will permit, similarly transferring an equal amount of second rinse into the first rinse tank, and making up the second rinse with water (note especially runs 8, 9, and 10, Table 3). This would eliminate the running rinse normally employed in tank 2.

Table 4 shows how the Hydranics stacks performed during one 7.5-hour period (following run 29, Table 1) after the plating line was shut down. Here it is seen that the first stage was removing only about one-fourth (66.7/242) of the average drag-out required to hold a steady concentration in the first rinse, and the second stage about three-fifths (10.7/16.9) of that required to stabilize the second rinse.

During this period of study, four main hypotheses were advanced (by various interested parties) to explain the relatively poor performance at Keystone on brass solutions as compared to that previously experienced on copper cyanide solutions. These were:

1. Physically defective membranes.

2. External current loss between electrodes in the first stage.

3. Poor flow distribution among chambers.

4. Some unexpected effect of the presence of zinc.

These hypotheses will be discussed individually.

Physically Defective Membranes

Obviously a hole of any sort in any one of the membranes will work against efficient dialysis. The ionac membranes employed were the standard materials MC-3470

and MA-3475. They were cut to approximate size, soaked in hot water, and then in cold water for several days. They were then die-cut to exact dimensions while wet. At this point they were inspected closely against a light source for pinholes, slits, or thin areas. The occurrence of such defects was rare, but when they were found, the membranes were rejected. Using this technique, there was the same degree of quality control exerted prior to cell assembly both before the pilot plant studies and before the Keystone Lamp work.

Further, newly assembled stacks were tested for internal cross-leaks (one cause of which would be perforated membranes) by passing water through one set of chambers at pressures up to 0.14 kg per sq cm while the other set of chambers was empty. Stacks were considered satisfactory if less than 5 cc per minute issued from the empty chambers.

Prior experience had shown that when membranes were damaged as a result of some serious malfunction, such as severe overheating by contact of membranes with an electrode (in earlier designs) or puncture of membranes by metal deposited on the cathode (before daily polarity reversal was introduced), there was no mistaking the condition. The concentrations of the two streams rapidly approached each other as complete mixing began to occur, and the levels in the two tanks feeding the stack would often rise and fall, respectively, at easily observable rates. When such a stack was subsequently tested hydraulically, the cross-leakage into an empty set of chambers would far exceed 5 cc per minute. Upon disassembly, visual inspection of the membranes usually would quickly reveal perforations.

Since none of these effects was observed for the runs described above, it seems most unlikely that the inefficiency of the cells at Keystone can be ascribed to physically defective membranes.

External Current Loss Between Electrodes in the First Stage

Two routes for current passage, other than through the stack, existed for the first stage. These were through the 0.635 cm feed lines and the 1.27 cm return lines to the electrode chambers, both carrying concentrated "bath" solution. The total distance from cathode (a point of origin on the feed line and thence to anode was nine feet. The corresponding return line loop was longer since it carried back to the recirculating drum and totalled 8.53 meters.

When the concentrated solution contained 50,000 ppm total cyanide, it had a conductivity of 280,000 μmhos/cm or a specific resistance of 3.6 ohm-cm. The current that would pass through these two routes is calculated as follows.

Current in feed line: $i_F = E/R_F$

$$R_F = \rho \times \frac{l_F}{A_F}$$

$$= \frac{3.6 \times 9' \times 12''/ft \times 2.54\ cm/in}{\pi \times 0.3^2}$$

$$= 3520\ ohms$$

$$i_F = E/R_F$$

$$= 125\ volts/3520\ ohms$$

$$= 0.036\ amperes$$

Current in discharge line: $i_D = E/R_D$

$$R_D = \rho \times \frac{l_D}{A_D}$$

$$= \frac{3.6 \times 20 \times 12 \times 2.54}{\pi \times 0.3^2}$$

$$= 2720\ ohms$$

$$i_D = E/R_D$$

$$= 125\ volts/2720\ ohms$$

$$= 0.046\ amperes$$

Total current through these routes:

$$i_F + i_D = 0.036\ amperes + 0.046\ amperes$$

$$= 0.082\ amperes$$

This is a very minor portion of the current passing through the first stage. No other possible routes of current loss could be found.

The same loops did not exist in the second stage because the solution supplied to the cathode chamber was always the dilute stream (second rinse) while that fed to the anode chamber was always the concentrated stream (first rinse).

Thus, it did not seem plausible that poor performance of the plant installation was due to failure of the current to pass through the stacks.

Poor Flow Distribution Among Chambers

It is well known that if the flow in one or more of the depleted chambers is appreciably reduced with respect to the others, the effects will be detrimental. The slower flow leads to greater de-ionization in the chamber involved, causing, in turn, lower amperage through the entire stack and less de-ionization of the other chambers. The over-all result, therefore, is less effective depletion.

The chamber design and assembly at Keystone was identical to that used in successful runs on sodium copper cyanide in the pilot plant, so that it was difficult to believe that flow distribution had become a problem between the two series of trials. Nevertheless, a means of shedding some light on the problem was afforded by the availability of the Asahi Glass Co. stacks. These cells had an altogether different type of distribution system and one which had been tested and found satisfactory over many years. Results obtained with the Asahi cells are discussed in the following section.

Some Unexpected Effect of the Presence of Zinc

The laboratory experiments designed to investigate the significance of this hypothesis are discussed later.

PERFORMANCE OF ASAHI STACKS ON BRASS PLATING SOLUTIONS

The data in Table 4 show an encouraging decrease in concentration of 1530 ppm CN/hr in the first stage depleting stream during the first day's run. However, the depleting stream in the second stage increased 66.6 ppm CN/hr during that run, as did both dilute streams for the next two days.

The rather high ▲ ppm CN/hr values for the second stage dilute stream are probably due to the correspondingly high concentration of the concentrating stream in that stage; it had not been possible to start the first rinse solution at as low a concentration as desired at the beginning of this trial.

Except for the short-lived (and as yet unexplained) good performance of the first stage during Run 1, it appeared that the Asahi cells were showing the same inefficiency in treating brass solutions, as compared to sodium copper cyanide solutions, as had been observed for the Hydranautics cells.

The operation of the two Asahi stacks in parallel on the first rinse alone is summarized in Table 5. As stated before, this arrangement ought to have improved depletion of the rinse because the effective membrane area was doubled without a

reduction in voltage per unit cell. The data for two runs shows there was no improvement. The respective increases in concentration were 130 and 389 ppm CN/hr.

With these results, one must conclude that either poor distribution of flow through the chambers is not a controlling factor in our observations on brass rinse treatment or that carefully designed cells are at present incapable of giving good enough uniformity of flow distribution. If the latter is true, then electrodialysis is of questionable technical feasibility. Success in other applications has long shown that this is not so.

Elimination of the aforementioned hypotheses concerning inefficient electrodialysis of brass solutions gave added impetus to exploration of the effect that zinc might have.

LABORATORY INVESTIGATIONS

Analysis of Anion Permeable Membrane from Brass E.D. Cell

The most obvious feature of the analytical data presented in Table 7 is that, while the amount of copper in brass plating solution is three times that of zinc, quite the reverse is true on the membrane where there is 1.5 times as much zinc as copper. The membrane evidently has a strong selectivity for zinc cyanide complex in this mixture or is a repository for a zinc oxide precipitate.

It may be pertinent to note that the sum of the number of milligram atomic weights of copper and zinc per gram of membrane is close to the ion exchange capacity of the membrane.

No. of mg at wts Cu/g membrane	0.284
No. of mg at wts Zn/g membrane	0.414
	0.698
Ion exchange cap. MA-3475, meq/g	0.743

This suggests that each complex metal cyanide anion may be attached by only about one negative charge per quaternary group on the membrane, leaving the remaining negative charges free to act as a "pathway" for migration of cations in the counter-direction through the membrane. The selectivity of the membrane for anion transport could thus be in large part destroyed and the entire electrodialysis process frustrated.

De Korosy and co-workers[6] found that ferrocyanide ion converted an anion permeable membrane into a cation permeable membrane, and that precipitates of certain metal oxides on membranes had similar effects. The writer believes that a phenomenon of this kind is at work in the electrodialysis of brass.

[6]De Korosy, F., et. al., J. Phys. Chem., 71, 3706 (1967); Desalination, 1970, 8 (2) 195-220 (C.A. 74, 25380 q.)

TABLE 7. CONCENTRATION OF COPPER AND ZINC IN ANION MEMBRANE MA-3475 AFTER USE IN BRASS ELECTRODIALYSIS: COMPARISON WITH BRASS SOLUTION

Item	Copper	Zinc
In Membrane:		
Weight %	1.8	2.7
Weight ratio	1.0	1.5
Number of mg atomic weights per g of membrane	0.284	0.414
Ratio of number of mg atomic weights	1.0	1.46
In Brass Plating Solution:		
Ounces/gallon	4.96	1.67
Weight ratio	2.97	1.0
Ratio of number of gm atomic weights	3.06	1.0

Membrane Resistance in Copper Cyanide and in Brass Solutions

The plots of amperes vs. volts for solutions and for cells containing membranes are shown in Figure 4. Note that the data for the solutions alone is nearly identical. If one observes the proximity of the circles to the crosses and x's, it is seen that a cation permeable membrane equilibrated with a brass solution adds very little to the resistance of the system used in this experiment. (The same was true of a cation permeable membrane equilibrated with sodium copper cyanide solution). This is not surprising because the ion exchange capacity of the cation membrane on a volume basis is fairly high and conductivity in these solutions is primarily due to the rapidly moving sodium ion.

On the other hand, the interposition of an anion membrane (equilibrated with sodium copper cyanide) between electrodes in a sodium copper cyanide solution raises the resistance considerably. An even greater increase in resistance is seen as a result of placing a brass-solution-equilibrated anion membrane between electrodes in the brass solution.

These experiments were felt to show that there was indeed a difference in behavior of anion membranes in copper cyanide and in copper, zinc cyanide solutions, although they did not in themselves explain the less efficient electrodialysis of brass solutions.

Small, Three-Chamber Cell Tests of Electrodialysis

These experiments were another attempt at a simplified demonstration of some difference between copper cyanide and brass solutions. In addition, sodium zinc cyanide solutions (without copper) were included in the work. The solutions studied are described in Table 8.

The course of typical electrodialysis runs is shown in Figure 5 where, at a constant 12 volts applied potential, the change of current with elapsed time is depicted.

In the case of both sodium copper cyanide and sodium zinc cyanide, there was a short initial rise in amperage, followed by a fairly rapid drop and a final levelling off. The concentrated brass solution showed an initial drop, followed by a long, gradual increase in current and then an almost symmetrical decrease; only after 110 minutes had the amperes decreased to the level (0.2 a) that the sodium copper cyanide and sodium zinc cyanide solutions had reached in 36 to 42 minutes. The diluted brass solution displayed no initial current rise, but only a gradual decline, reaching 0.29 a in 61 minutes.

The slow rate of current fall in the case of the brass solutions indicates slow depletion of the center chamber, and this is shown quantitatively in the analyses recorded in Table 9. The column headed Δ ppm/hr shows that the rate of concentration decline with time in the brass solution is only about one-quarter to one-half that in the

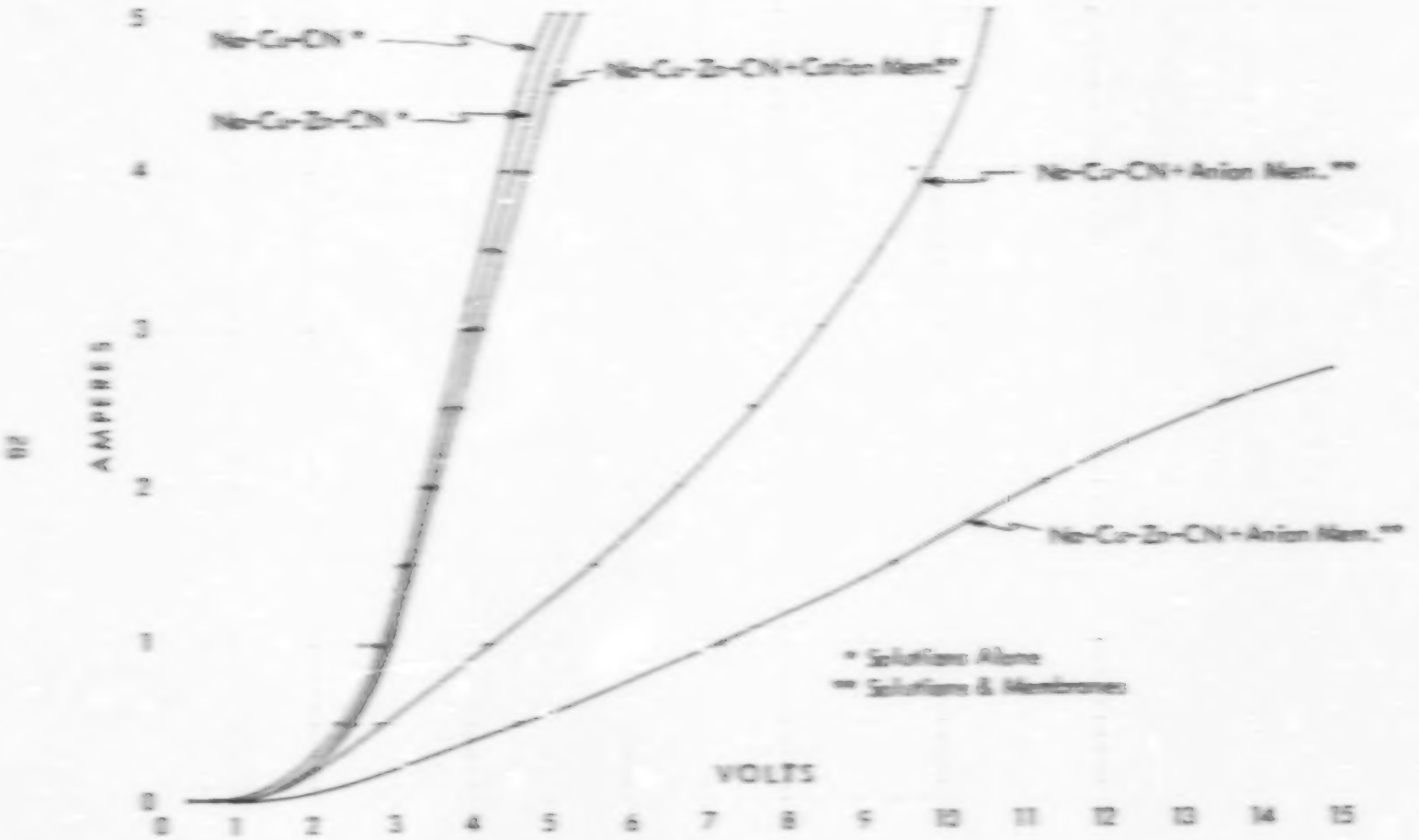

Figure 4. D.C. Amperes vs. Applied Voltage

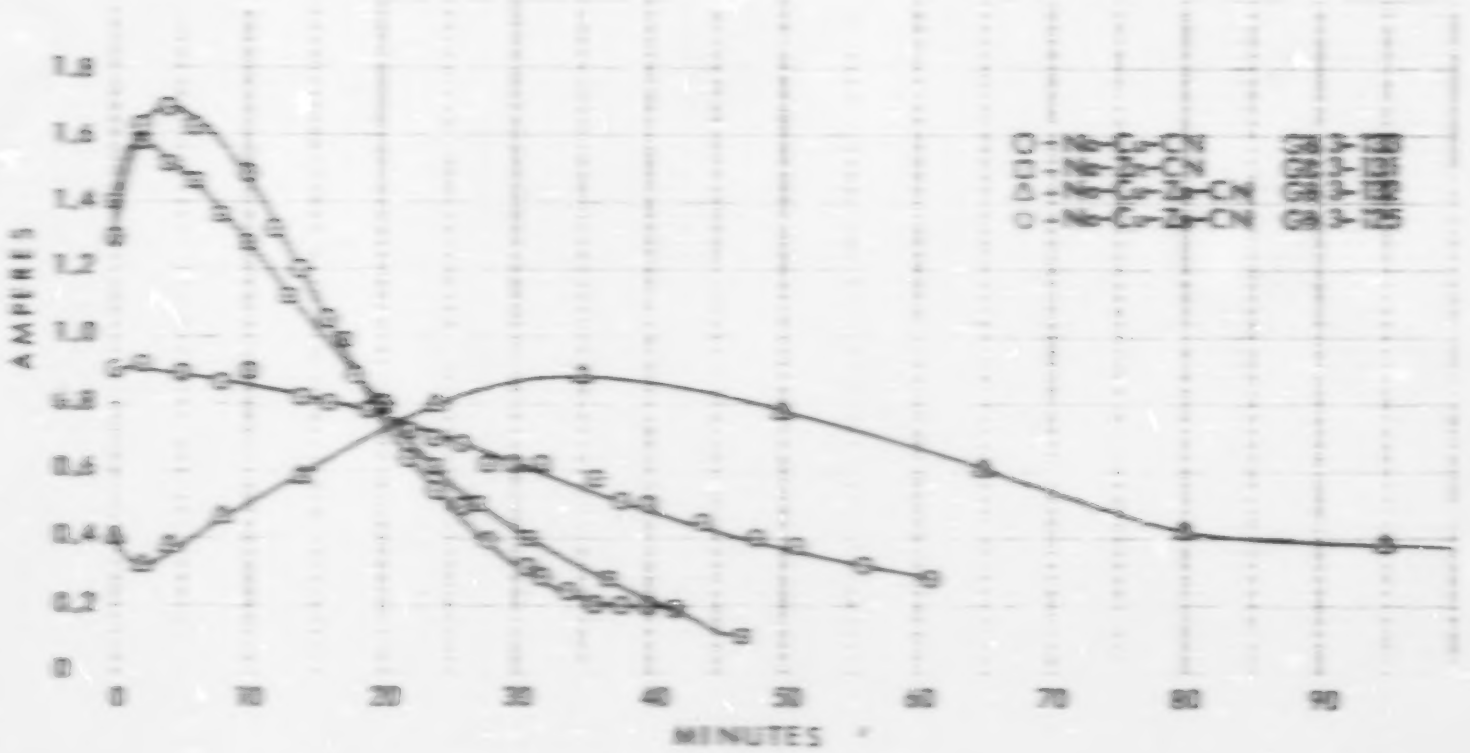

Figure 5. Three-Chamber Cell Electrodialysis, Amperes vs. Minutes

TABLE 8. THREE-CHAMBER CELL ELECTRODIALYSIS CHARACTERISTICS OF COPPER, ZINC, AND BRASS SOLUTIONS

Run No.	Components	Composition of Electrode Chambers (oz/gal) CuCN	$Zn(CN)_2$	NaCN	Ratio of Concentration Center Ch./Electr. Ch.	Time of Run (minutes)	Conductivity of Center Chamber (μmhs/cm) Start	Finish
GB-3-133	Na-Cu-CN	16	0	18	1/50	42	5900	460
GB-3-131	Na-Zn-CN	0	15	17	1/50	47	4900	600
GB-3-132	Na-Cu-Zn-CN	10	5.5	14*	1/50	110	8000	1300
GB-3-125	Na-Cu-Zn-CN	5	2.75	7†	1/50	61	4900	1240

* Keystone Brass Plating Solution – Also contains 1 oz. NaOH/gal.

† Keystone Brass Diluted 1:1 with Water.

TABLE 9. THREE-CHAMBER CELL E.D. CONCENTRATION CHANGES

Item	Start	Finish	Finish / Start x 100 (%)	Δ ppm	Δ ppm
133-Cu:					
Cond.	5900	460	7.8	-	-
Cu	1700 mg/l	92	5.4	1608	2300
Na	1200	85	7.1	1115	1640
CN	3050	150	4.9	2900	4150
pH	10.3	9.8	-	-	-
131-Zn:					
Cond.	4900	600	12.2	-	-
Zn	1100	100	9.1	1000	1280
Na	1050	105	10.0	945	1210
CN	2450	450	18.4	2000	2560
pH	11.0	10.3	-	-	-
132-Cu, Zn:					
Cond.	8000	1100	13.75	-	-
Cu	840	70	8.3	770	420
Zn	900	50	10.0	450	245
Na	1700	180	10.6	1520	830
CN	2850	350	12.3	2500	1360
pH	11.1	9.5	-	-	-

sodium copper cyanide solution, depending on which species of ion is compared. Similarly, the calculations shown below for the following Table 10 indicate a lower efficiency of electrodialytic depletion of all species of ions from a brass solution as compared to a sodium copper cyanide solution.

TABLE 10. EFFICIENCY OF ELECTRODIALYTIC DEPLETION

Element	% Ampere Efficiency for Ion Depletion	
	Na-Cu-CN Solu.	Brass Solu.
Na	47.4	38.5
Cu	47.4	13.4
Zn	-	7.6
CN	104.5	53.1

The amperes vs. minutes curve for the sodium zinc cyanide solution is quite close to that for the sodium copper cyanide solution, but the analytical data and ampere efficiency calculations lie between the values for the copper solution and the concentrated brass solution. The writer can offer no explanation for this.

In general, the writer believes that the laboratory experiments have shown that there is enough difference between sodium copper cyanide and brass solutions to account for the difference observed in the performance of the Hydrantes and Asahi E.D. stacks when operating on these two solutions. To determine exactly the mechanism by which brass solutions cause poorer efficiency of electrodialysis is beyond the scope of this project. We can only suggest that the effect must be due to a phenomenon like one or more of those observed by De Korosy, mentioned above.

Calculations

Faraday — 96,500 amp-secs
1,608 amp-min
1 Milli-Faraday = 1,608 amp-min transports 1 meq

133-Cu

amp-min = 34.28
milli-F = 21.35

▲ mg/l Na 1115 x .2 = 223.0 mg
÷ 22
10.1 meq Na

▲ mg/l Cu 1600 x .2 = 321.6 mg
÷ 31.8
10.1 meq Cu*

▲ mg/l CN 2900 x .2 = 580 mg
÷ 26
22.3 meq CN

AE (Na) = $\frac{10.1}{21.35}$ = 47.4 %

AE (Cu) = $\frac{10.1}{21.35}$ = 47.4 %

AE (CN) = $\frac{22.3}{21.35}$ = 104.5 %

131-Zn

amp-min = 34.56
milli-F = 21.5

▲ mg/l Na 945 x .2 = 189.0 ÷ 22 = 8.6 meq Na
▲ mg/l Zn 1000 x .2 = 200 ÷ 32.7 = 6.1 meq Zn*
▲ mg/l CN 2000 x .2 = 400 ÷ 26 = 15.4 meq CN

AE (Na) = $\frac{8.6}{21.5}$ = 40.0 %

AE (Zn) = $\frac{6.1}{21.5}$ = 28.3 %

AE (CN) = $\frac{15.4}{21.5}$ = 71.5 %

(continued)

* Assuming the migrating anions are principally $Cu(CN)_3^=$ and $Zn(CN)_4^=$

Calculations --(Continued)

132-Cu, Zn

amp-min = 98,21
milli-F = 36,2

▲ mg/l Na 1520 x ,2 = 304 ÷ 22 = 13,9 meq Na
▲ mg/l Cu 770 x ,2 = 154 ÷ 31,8 = 4,85 meq Cu*
▲ mg/l Zn 450 x ,2 = 90 ÷ 32,7 = 2,75 meq Zn*
▲ mg/l CN 2500 x ,2 = 500 ÷ 26 = 19,2 meq CN

AE (Na) = $\frac{13,8}{36,2}$ = 38,2 %

AE (Cu) = $\frac{4,85}{36,2}$ = 13,4 %

AE (Zn) = $\frac{2,75}{36,2}$ = 7,60%

> AE(Cu & Zn) = 21,0%

AE (CN) = $\frac{19,2}{36,2}$ = 53,1 %

* Assuming the migrating anions are principally $Cu(CN)_3^{=}$ and $Zn(CN)_4^{=}$